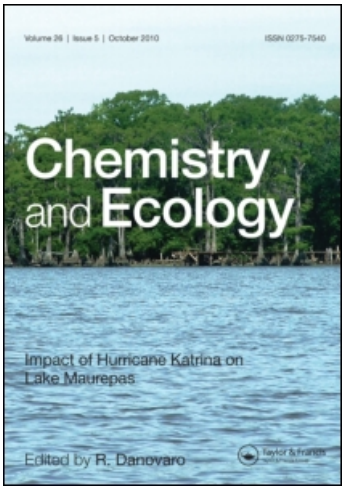

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Water quality in a mediterranean marine protected area (North Sporades Islands, Greece)

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WATER QUALITY IN A MEDITERRANEAN MARINE PROTECTED AREA (NORTH SPORADES ISLANDS, GREECE)

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Pollution in the marine protected area of North Sporades Islands was investigated in July 1997. Salinity, temperature, dissolved oxygen, dissolved inorganic nutrients, organic carbon, hydrocarbons as well as dissolved and particulate trace metals were determined at 15 offshore and coastal stations. Dissolved organic carbon and inorganic nutrient concentrations indicate the mesotrophic character of the investigated waters. The dissolved forms of nitrogen were slightly higher at coastal stations. Dissolved and particulate Cu, Zn and Ni, were higher in coastal stations, whereas concentrations of Pb were generally low and likely of atmospheric origin. Dissolved/Dispersed petroleum hydrocarbons (DDPH) were close to detection limits at all stations. Temperature and salinity vertical profiles, nutrient and trace metal concentrations revealed the presence of a slight influence of the Black Sea water coming from Dardanelles straits.

Keywords: Marine protected areas; Nutrients; Heavy metals; Hydrocarbons; Sporades

1 INTRODUCTION

A marine park or marine protected area (MPA) is a designated area, which usually includes a stretch of coast, as well as sea and constitutes a fragile ecosystem characterized by a relevant biological diversity, interesting geological structure and/or important cultural elements. The area is subjected to specific legislation which aims at protecting and conserving rare habitats and threatened species (IUCN, 2000). The creation of the National Marine Park of the North Sporades Islands (Greece) has the following aims:

- The protection, conservation and management of the wildlife and landscape which constitutes natural heritage and a valuable national natural resource, in extended terrestrial and sea areas of the N.Sporades.
- The protection of one of the most important habitats of the Mediterranean monk seal *Monachus monachus*, a species threatened to extinction. It is estimated that only a few hundred individuals remain scattered over the whole of the Mediterranean. The largest population of seals is found in Greece spread out over the Aegean Sea. Because of its morphology and position, the area of the Marine Park is an ideal habitat for seals.

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- The protection of other rare and threatened plant and animal species which find refuge in the islands.
- The development of the region by the sustainable use of its natural resources.

The aim of the present study that deals with pollution levels of the Marine Protected Area of North Sporades Islands is the collection of background information that can be used as a basis for the sustainable management of the MPA. This is the first research carried out on this subject in the area. Hydrological parameters (salinity, temperature, dissolved oxygen) and pollutants (including nutrients, organic carbon, petroleum hydrocarbons and heavy metals) were determined in order to quantify the influence of human activities on this marine system.

2 THE STUDY AREA

The National Marine Park of North Sporades (Fig. 1) was founded in Greece by Presidential Decree (G.G. 519/92) on 28/5/1992. Alonnissos is the largest island in the park, which also encompasses six smaller islands (Peristera, Kyra Panagia, Gioura, Skantzoura, Piperi) and 22 uninhabited islands and rocky outcrops.

The total population of the area is about 3000 persons. There are two protected zones: Zone A (1587 km^2): the zone of strict protection. The approach to this area requires special permission and hunting is strictly forbidden. There are not inhabited islands there. Zone B (678 km^2), open to visitors. There are no specific restrictions except of the free camping and lighting of fires. The morphology of the area, the limited degree of human interference and the excellent

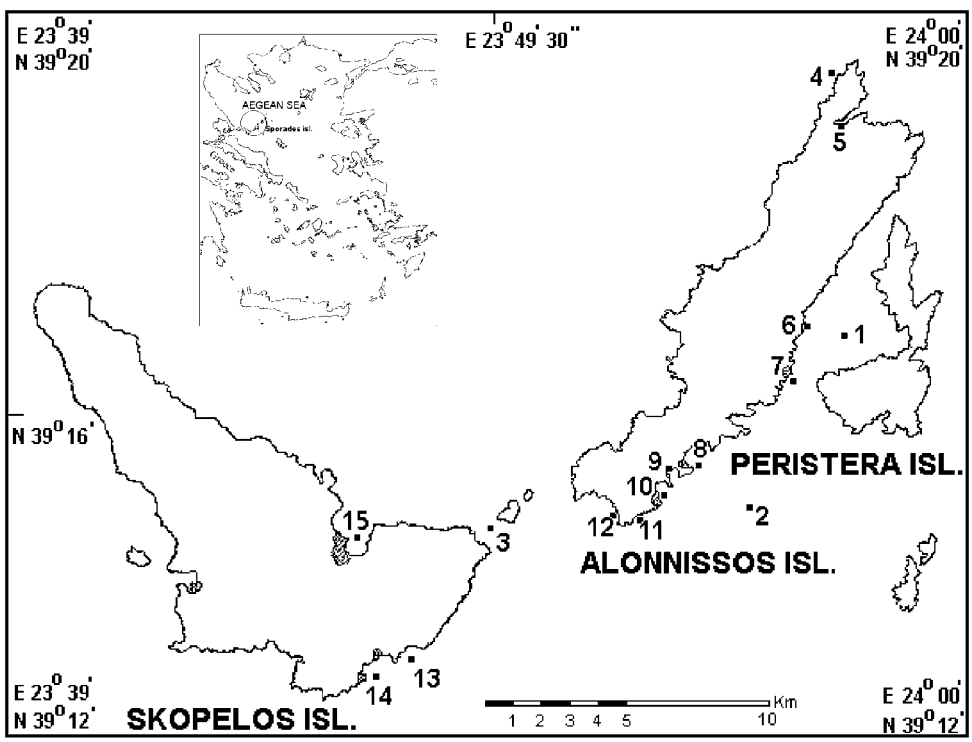

FIGURE 1 The studied area and the sampling stations.

environmental conditions make the park an ideal habitat for several threatened plant and animal species. Underwater fauna includes several benthic and fish species. Besides the presence of monk seals, various species of dolphins and some whale species are present. There are widely spread *Posidonia oceanica* beds in excellent condition. The climate is of Mediterranean type with a wet winter and dry summer with an average annual temperature of 17 °C and the average annual rainfall is 515 mm. No monitoring systems are present in the area, although its environmental significance is recognised (Dassenakis *et al.*, 2001).

3 MATERIALS AND METHODS

The study was carried out in July 1997. During summer the region is under maximum environmental pressure due to increased population (ca double than in winter) and shipping. Surface water samples were collected at 15 stations as shown in Figure 1. A synoptic description of these stations is also given in Table I. Samples were divided into 4 groups according to their geographical position and depth:

1. The surface samples of offshore stations 1, 2, and 3.
2. The samples collected from 30 m depth (below the thermocline) of the offshore stations 1, 2, and 3.
3. The coastal stations 4 to 12, around the island of Alonnissos.
4. The coastal stations 13, 14, and 15, around the island of Skopelos.

Temperature, dissolved oxygen, pH and salinity were measured *in situ* by the CTD system AQUA-16 that was calibrated before use with standard solutions.

Seawater samples were collected by Hydro-Bios polypropylene bottles and were filtered through pre-weighed 0.45 μm Millipore membrane filters. All samples were handled in a laminar flow bench in order to avoid any contamination.

For the determination of particulate metals, the particulate material, retained on filters, was dried to constant weight and treated into PTFE beakers with concentrated HNO_3 at 200 °C to dissolution. Dissolved trace metals were pre-concentrated on Chelex-100 resin (Riley and Taylor, 1968) and then eluted with a mixture of 2N:1N HNO_3:HCl (Scoullos and

TABLE I Description of Sample Stations.

Station number		*Depth (m)*
1	Alonnissos/Vasiliki (Between Alonnissos Isl. and Peristera Isl.)	80
2	Offshore/Alonnissos (SE)	56
3	Channel between Alonnissos and Skopelos Isl.	34
4	Alonnissos/Analipsi	9
5	Alonnissos/Geraka bay	1
6	Alonnissos/Kalamaki bay	1
7	Alonissos/Steni Vala	1
8	Alonissos/Votsi bay	1
9	Alonissos/Rousoum Gialos bay	1
10	Alonnissos/Harbour	1
11	Alonnissos/Spilia	1
12	Alonnissos/Marpounta bay	1
13	Skopelos/Mpelano	5
14	Skopelos/Stafylos	10
15	Skopelos/Harbour	2.5

Dassenakis, 1984) after the removal of Ca and Mg with ammonium acetate pH 5 (Kingston *et al.*, 1978). The resin was used in NH_4^+ form and the flow rate to 3 ml min^{-1}. These conditions give the best recovery (over 98%) of trace metals (Dassenakis and Scoullos, 1992; Rapti, 2000). Finally trace metals were determined by the use of both flame and flameless atomic absorption spectrophotometry using a VARIAN SpectrAA 200 instrument (Flame AAS) and a VARIAN SpectrAA 640Z instrument (Graphite Furnace AAS) with Zeeman background correction.

Spectrophotometric methods were used for the determination of inorganic nutrients (NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}, SiO_4^{4-}) (Grasshoff and Kremling, 1997). A UV–Vis spectrophotometer VARIAN Cary 1E was used for this purpose.

Dissolved Organic Carbon was determined by a TOC analyzer SHIMADZU 5000A.

Fluorescence spectroscopy was used for the determination of dissolved and dispersed petroleum hydrocarbons (DDPH) using a PERKIN-ELMER 512 double beam fluorescence spectrometer. The pretreatment of the samples included extraction with *n*-hexane and condensation by a rotary evaporator. The results are expressed in terms of "Chrysene equivalents" (Gordon and Keiser 1974; IOC Manuals and Guides No. 13).

All used methods have been tested in the laboratory for their accuracy and reproducibility using reference materials and replicate samples (Rapti, 2000; Ladakis, 1998; Botsou, 1997). The relative standard deviations (as coefficient of variation) of the various determinations were the following: NO_2^- (2.5), NO_3^- (4.2), NH_4^+ (7.8), PO_4^{3-} (5.5), SiO_4^{4-}(2.8), TOC (2.4), DDPH (8.9), Dissolved Cu (4.1), Particulate Cu (3.8), Dissolved Zn (4.6), Particulate Zn (5.5), Dissolved Ni (5.8), Particuate Ni (3.8), Dissolved Pb (6.7), Particulate Pb (5.9).

4 RESULTS AND DISCUSSION

Vertical profiles of the main hydrological parameters at station 1 (Fig. 2) indicate the existence of a well-established thermocline between 10 and 20 meter depth. An opposite trend was observed for salinity that displayed a clear alocline between 10 and 18 meter depth with surface values about 20% lower than those below. As the high summer temperatures in the area

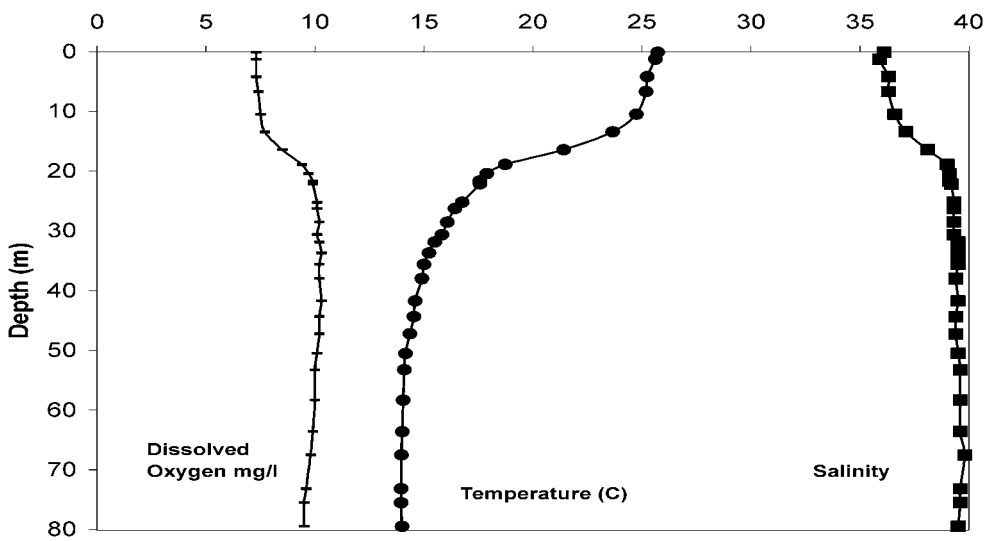

FIGURE 2 Vertical profiles of temperature, salinity and dissolved oxygen at station 1.

(about 30 °C) in combination with the absence of any inflow of fresh water should lead to increased evaporation and high surface salinity, our data suggest a possible influence by water masses of lower salinity having different origin probably from Black Sea. In this regard it has been reported that Black Sea waters might come into the western part of the North Aegean through Dardanelles straits (Zodiatis, 1994; Barbetseas, 1999; Latif and Ozsoy, 1999).

The seawater was almost saturated in dissolved oxygen, though values were slightly lower in the upper water layer. The pH fluctuation was limited (8.17–8.26).

The ranges and mean values of the concentrations of nutrients (NO_2^-, NO_3^-, NH_4^+, SiO_4^{4-} and PO_4^{3-}) and dissolved organic carbon (DOC) are presented in Table II. In Figure 3 are illustrated the mean total nitrogen concentrations and the percentage of NO_2^-, NO_3^-, NH_4^+, in various sample groups. The maximum values of nitrates and ammonia (>2 μM N) were measured at stations 8, 9 and 12 along the coast South of Alonnissos, near touristic beaches. At these stations the highest concentrations (>2 ppm) of Dissolved Organic Carbon (DOC) were measured.

At stations 1, 2 and 3 the mean values of ammonia were similar in surface and below the thermocline as tested using the One Way Analysis of Variance (One Way ANOVA) at the significance level 0.05. On the other hand the surface concentrations of NO_3^- exceeded the ones below the thermocline for about 30%. At stations 1, 2 and 3 the percentages of NO_2^- were very limited, but the mean percentage of NO_3^- and NH_4^+ were similar in surface samples. This is an unusual phenomenon in open seas, as NO_3^- is the prevailing dissolved form of N in surface well-oxygenated waters. The contribution of NH_4^+ was dominant on NO_3^- in samples taken below the thermocline and near the coast of Skopelos, whereas the opposite was observed near the Alonnissos coast. The contribution of nitrites near Skopelos, although very low, was also higher than near Alonnissos. The general view of the concentrations of nitrogen micro-nutrients indicates that the marine environment (and particularly the coastal one) is affected by human polluting activities (Riley and Chester, 1971a). The concentrations of PO_4^{3-} were generally low. The highest values (>0.2 μM P) were measured at coastal stations 10, 11 and 12 in the touristic area of South Alonnissos. The mean values of SiO_4^{4-} were similar at the four groups of samples. Highest values (>1 μg M Si) were measured at stations 5, 6, 7 and 15 along the coasts of North Alonnissos. The stations displaying increased nitrogen and phosphorus concentration are different from those displaying increased silicate concentration. Such differences indicate that the coastal environment represents a nutrient sources responsible for higher levels of nitrogen and phosphorus.

According to the criteria of Karydis and Coccossis (1990), based on the concentrations of inorganic nutrients, our data indicate that the area is in the upper mesotrophic level (Karydis, 1992). This conclusion differs from the general assumption dealing with the oligotrophic characteristics of the Aegean Sea (Dassenakis *et al.*, 2000), but is consistent with the mesotrophic level reported for coastal areas of Rhodos island, similarly interested by touristic pressure (Karydis, 1992).

In the study area the wide dispersion of the values of N/P ratios do not allow calculating a mean value to be compared with the Redfield ratio 15:1 (Riley and Chester, 1971b). According to the criteria proposed by Justic (1995) based on the combination of the ratios of inorganic Si, P and N Si appears the most probable limiting factor for phytoplankton growth because the Si/P ratios are lower than 10 and the Si/N ratios are lower than 1 in twelve of the eighteen samples analysed.

Nutrient concentrations from various areas of the Aegean Sea are reported in Table III. A comparison between them and our data reveals that, as far as nitrates, ammonia and phosphates are concerned, North Sporades' values are higher than those typical of the open Aegean Sea and open Mediterranean Sea and lower than those reported for polluted areas such as Saronikos and Euvoikos gulfs.

TABLE II Mean Values and Ranges of Nutrients in the Four Groups of Samples.

		NO_2^- (μmol N/l)	NO_3^- (μmol N/l)	NH_4^+ (μmol N/l)	Total N (μmol N/l)	PO_4^{3-} (μmol P/l)	SiO_4^{4-} (μmol Si/l)	Diss. Org. C (mg C/l)
Group 1 (Surface of deep stations)	Average	N.D.*	0.98	0.96	1.93	0.07	1.20	1.59†
	Range	N.A.	0.64–1.30	0.24–1.86	0.88–3.16	0.01–0.11	0.14–3.29	1.48–1.71†
Group 2 (30 m depth of deep stations)	Average	0.02	0.72	0.93	1.67	0.09	0.85	1.33
	Range	0.01–0.04	0.44–1.17	0.63–1.23	1.08–2.44	0.06–0.11	0.61–0.99	1.24–1.39
Group 3 (Coasts of Alonnissos)	Average	0.03	1.82	1.18	3.04	0.15	0.85	2.85
	Range	0.00–0.15	0.30–3.85	0.33–2.51	0.63–5.79	0.01–0.31	0.17–1.57	1.01–6.11
Group 4 (Coasts of Skopelos)	Average	0.05	0.34	1.20	1.58	0.08	0.80	1.39
	Range	0.00–0.10	0.26–0.39	1.00–1.42	1.39–1.83	0.04–0.13	0.32–1.25	0.98–1.84
Total mean values		0.03	1.25	1.11	2.38	0.12	0.90	2.18†

*N.D. = C < 0.005 µmol/l. N.A. = Not Available.

†Surface sample of sample station No 3 not included due to the very high value when compared to the others (21.33 mg/l).

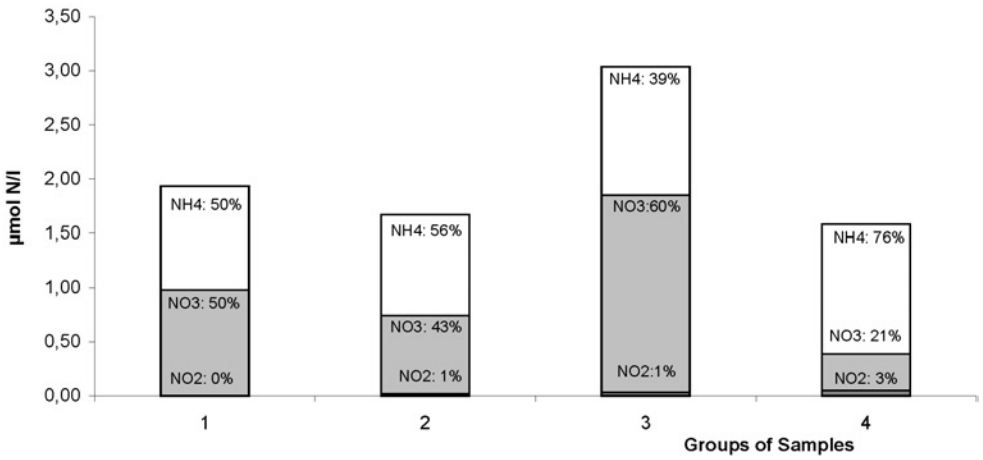

FIGURE 3 Distribution of dissolved inorganic nitrogen in the four groups of samples (1: Surface of deep stations, 2: 30 m depth of deep stations, 3: Around Alonnissos, 4: Around Skopelos).

As far as levels and distribution of trace metals is concerned (Fig. 4), the main conclusions coming from our measurements are the following: the dissolved phase of metals predominates over the particulate one. The mean percentages of dissolved metals relatively to the total metal concentration were 60% for Cu, 82% for Zn, 92% for Ni and 80% for Pb. It is a rather common phenomenon in open seas (such as the Aegean Sea) to have a limited suspended load and thus low particulate matter concentrations (Riley and Chester, 1971c).

Highest concentrations of Cu, Zn, Ni in both dissolved and particulate phase, were observed under the thermocline. This suggests that there were no major metal sources in coastal areas and, probably, the organic matter decomposition under the thermocline represents the main source. The opposite trend (increased values at surface waters) is observed for Pb concentrations. This is probably due to the well-known atmospheric origin of this element in the whole Mediterranean area (Guerzoni *et al.*, 1999).

TABLE III Mean Values of Nutrients in Various Areas (Values in µmol/l).

	NO_2^-	NO_3^-	NH_4^+	PO_4^{3-}	SiO_4^{4-}	*Reference*
Saronikos Gulf 1995	0.13	1.46	1.23	0.24	3.45	NCMR (MedPol Report, 1996)
Pagassitikos Gulf 1990	0.18	0.72	0.36	0.22	2.10	Papaevagelou (1993)
Outer Saronikos Gulf 1995	0.18	0.42	0.78	0.09	1.52	Psilidou *et al.* (1995)
Rhodes Island August 1998	0.03	0.96	1.49	0.31	–	Corsini-Foka *et al.* (2000)
Central Euvoikos Gulf 1998	0.18	5.81	2.71	0.22	8.14	Dassenakis *et al.* (1999)
N.Aegean Sea 1992–94	0.04	0.84	0.34	0.07	1.65	Kucukszgin (1995)
S.Aegean Sea 1992–94	0.03	0.78	0.28	0.06	1.83	Kucukszgin (1995)
Mediterranean Sea	0.16	0.42	0.36	0.12	1.22	Friligos (1987)
Present study	0.03	1.25	1.11	0.12	0.90	

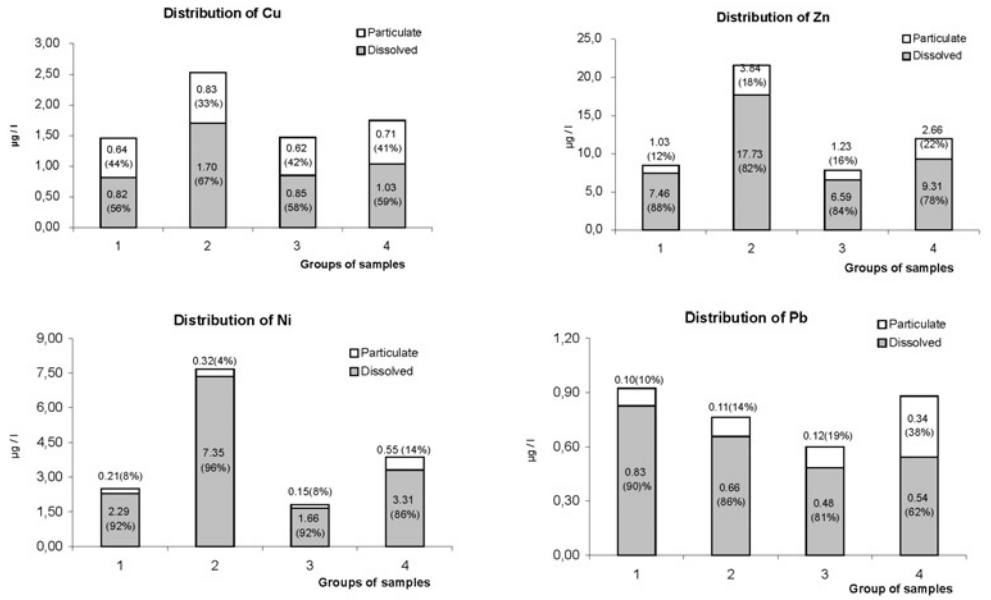

FIGURE 4 Distribution of dissolved and particulate Cu, Zn, Ni and Pb in the four groups of samples (1: Surface of deep stations, 2: 30 m depth of deep stations, 3: Around Alonnissos, 4: Around Skopelos).

In surface water close to Skopelos higher metal concentrations than in Alonnissos were measured, probably because of the increased shipping in these areas. The comparison of metal values in North Sporades with various areas of the Aegean sea (Tab. IV) reveals that concentrations of Cu and Zn and Ni were rather high if we consider that in this area there are not apparent metal sources. There is likely a diffused pollution in the whole area of western Aegean Sea, probably coming from the Black Sea and the Greek

TABLE IV Mean Values of Metals in Various Greek Marine Areas (Values in µg/l).

	Cu		*Zn*		*Ni*		*Pb*		
	Diss	*Part*	*Diss*	*Part*	*Diss*	*Part*	*Diss*	*Part*	*Reference*
Saronikos Gulf 1986–93	1.25	0.27	N.A.	N.A.	3.07	0.70	0.94	0.15	Scoullos *et al.* (1994)
Elefsis Gulf 1986–93	1.52	0.60	N.A.	N.A.	4.75	1.04	1.08	0.26	Scoullos *et al.* (1994)
Maliakos Gulf 1982–86	0.76	0.30	3.53	1.71	2.85	1.62	0.63	0.32	Scoullos *et al.* (1986)
Central Euvoikos Gulf 1998	0.80	0.30	8.64	1.45	N.A.	N.A.	1.25	0.32	Dassenakis *et al.* (1999)
E.Aegean Sea 1980	0.90	0.40	6.00	1.00	1.20	0.10	1.30	0.40	Scoullos *et al.* (1984)
Saronikos Gulf 1999	0.48	0.16	2.23	N.A.	0.45	0.08	0.52	0.17	Tsorova (2000); Gourioti (2000)
Outer Thermaikos Gulf 1997	0.18	0.04	N.A.	N.A.	0.34	0.06	N.A.	N.A.	Zeri *et al.* (2000)
N.Aegean Sea 2000	0.19	N.A.	N.A.	N.A.	0.41	N.A.	N.A.	N.A.	Voutsinou *et al.* (2000)
Present study	1.03	0.68	9.19	1.91	3.06	0.26	0.58	0.15	

N.A. = Not Available.

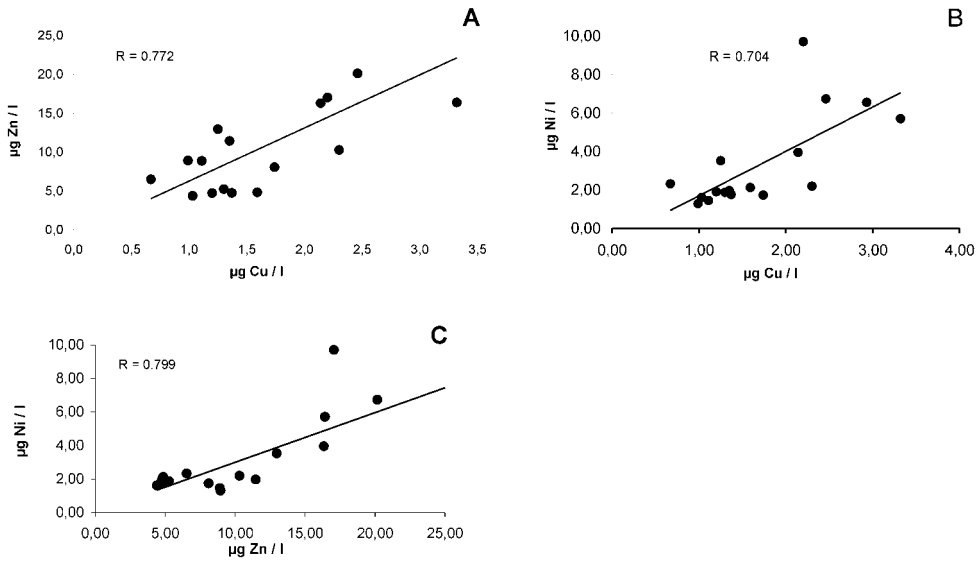

FIGURE 5 Correlation between the total concentration of Cu, Zn and Ni. A: Cu/Zn, B: Cu/Ni, C: Zn/Ni.

Mainland (industrial areas in Thessaloniki), which is transferred to the area of North Sporades by currents (Lascaratos, 1992; Zodiatis, 1994). In addition, is likely that pollution might be also caused by shipping activities. On the other hand, Pb concentrations, in both dissolved and particulate form, are remarkably lower than in other areas. However, since these measurements have been carried out in different years, this is a possible consequence of the decreasing use of lead-gasoline in Greece during the last years.

In Figure 5 the total (dissolved plus particulate) concentrations of Cu, Zn and Ni are significantly correlated. Positive trends indicate similar behavior and sources of these metals. On the contrary, such trend was not observed for Pb concentrations.

Measurements of DDPH in surface samples are presented in Table V. The values were found to be very low at all stations, except of station 8. The mean concentration of DDPH in the area of North Sporades is lower than at most marine regions reported in Table VI. DDPH levels are consistent with reducing trend observed in Greek coastal areas in the last years.

TABLE V Concentration of DDPH.

Sampling station	*Concentration (µg/l in Chrysene equivalents)*
1 (surface)	0.21
3 (surface)	0.05
4	0.09
5	N.D.*
8	3.07
15	0.16
Average	0.10†

*N.D. = C < 0.005 µg/l.
†Station No 8 not included.

TABLE VI DDPH Values in Greek Marine Areas (μg/l in Chrysene Equivalents) (from Dassenakis *et al.*, 2000).

Area	*Range*	*Mean values*
East Aegean Sea (1983)	0.14–1.39	0.86
East Aegean Sea (1983–1986)	0.09–5.9	
East Aegean Sea (1986–1989)	0.09–25.5	
North Aegean Sea		2.90
Saronikos Gulf 1981	1.6–5.6	
Ismir Bay (1983)	0.75–9.4	
South Euvoikos gulf (1997)	<0.04–0.49	0.17
Chios island	1.3–2.5	
Rodos island	2.0–3.7	
North Crete (1997)	0.09–0.32	
Lesvos island (1996)	0.09–9.60	2.05
Ag. Nikolaos (Crete) 1996	0.02–3.47	1.60
Present study	< 0.005–0.21	0.10

5 CONCLUSIONS

The National Marine Protected Area of North Sporades is of high ecological and environmental significance. The implementation of the environmental legislation, relative to the foundation of Marine Park, is not adequate yet, and the area, especially in Zone B, is affected by pollution sources. Results presented here (July 1997) are the first available and indicate the mesotrophic characteristics of the coastal area of Skopelos and Alonnissos. A still low anthropogenic impact is evident from Cu, Zn, Ni and NH_4^+ concentrations. A moderate influence of the Black Sea waters is apparent in the North Sporades area. A monitoring system, including seasonal samplings, has to be established in the area, covering at least eight coastal and offshore stations (Dassenakis *et al.*, 2001) in order to monitor the health state of these ecosystems and to plan future intervention in case of accidental pollution.

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